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REPORT OF AATCC SUBCOMMITTEE ON TRANSFERENCE OF COLOR

To Research Committee Meeting at Providence, March 23, 1945.

THE committee believes that the methods at present shown in the current Year Book for rating color transference and crocking may now be improved upon from the standpoints of accuracy, ease of application and consistency. It is noted that although Army and Federal specifications in many cases have adopted AATCC fastness tests and rating methods as the best available, in the case of crocking, the most recent Quartermaster Corps Specifications on "Test Methods for Textiles," P.Q.D. No. 447A, dated January 19, 1945, uses the AATCC Crockmeter, but for evaluation employs the Munsell Gray Scale by one-half steps from 9.0 to 6.5, and supplies the necessary Munsell chips. Likewise in J.Q.D. No. 623, dated February 2, 1945, on "Duck, Nylon, Spun, Yarn," a rating of 7 or better on the Munsell gray scale is required for fastness to crocking, on an OD 7 shade.

We consider the use of the Munsell gray scale as an advance over the current AATCC method using three selected worsted dyeings, varying in degree of crocking fastness, as standards of comparison, but believe that a higher degree of rating precision and consistency can be attained for the entire gamut of dyed materials by including, with the neutral grays, ranges of various hues of equal Munsell value. Our tests showed that the rating of crocking spots can be accomplished with greater ease and better consistency if visual comparison is made between related hues, even though they do not exactly match.

Consideration was also given to the use of other instruments, which measure brightness, for this purpose, but it was decided that they did not fulfill all requirements for this application, and when used without colored filters would give results corresponding to the visual use of the Munsell gray scale only. With the use of filters selected for the hues coming into question, it was felt that the operation and interpretation would become too complicated. The Polaroid device made by Mr. Walter Durfee was also considered, and while ingenious and useful for some applications, was thought not entirely suitable for our purpose, chiefly because of difficulty of comparison with test pieces and because it also measures in terms of varying depths of gray.

Using the Munsell chips, it was at first hoped that 2 ranges of 6 colors, namely at value 9, chroma 1, and at value 8, chroma 2 might suffice for rating crocking fastness on a 1-5 scale, the rating of 1 to be given to tests lower in brightness than the 8/2 group. However, after further study, and considering that many commercial dyeings, for example, dyed with Indigo, Naphthols, and Chrome Blacks, would thus be rated as 1, although they have been accepted by the trade as representing the best obtainable in these categories, it was found necessary to include a third range, namely value 7, chroma 2, which, similar to the 9/1 and 8/2 ranges, would include the gray, red, yellow, green, blue and purple colors. The rating method proposed, as applied to crocking tests, carried out on the Crockmeter by the usual technique (10 revolutions or 20 strokes) is as follows:

	Rating
Practically unstained	5
Equal to 9/1	4
Equal to 8/2	3
Equal to 7/2	2
More heavily stained than 7/2	1

Fractional or decimal values between these figures can be interpolated by the observer.

A series of 9 crocking tests of various hues and intensities was rated independently by seven committee members using this method, and the ratings so obtained showed good agreement within one-half unit from the averages, both when viewed by daylight and by artificial light.

It is suggested that the 3 value ranges of 6 colors each be mounted in 3 rows on a white card, with 12 holes slightly smaller than the crock test spot punched in the mounting card between the rows of ships. In this form the card can be used directly for comparison of test samples, or if desired, the user may make a two-hole mask for comparing equal areas of test piece and standard while masking out adjacent chips. In addition for some applications the user may prefer to cut up the mount so that each of the 3 value ranges of 6 colors is on an individual strip. A cloth hinged cover card would protect the chips against soiling. Instructions for operation and evaluation should be printed on the card, without reference, however, to the Munsell nomenclature. Such an arrangement should be quite inexpensive and easily assembled by a sample card manufacturer. Reproducibility should also be simple, due to the fundamental character of the Munsell chips.

With reference to the procedure for carrying out crocking tests, it is suggested that the cotton material have a degree of whiteness equivalent to Munsell value 9.3-9.5, and we would recommend brushing the completed test before rating in order to remove loosely adhering colored fibers.

If the proposed evaluating method is adopted, it would probably be desirable to rate the present three crocking standards according to the new method and to publish the values so obtained, in order to assist those who have become established on the present system.

Our investigations so far have been directed chiefly toward providing an evaluating method for crocking tests; we believe, however, that the yardstick proposed will serve equally well for measuring all cases of color transference, such as sublimation, perspiration, water, damp hot pressing, washing and peroxide tests, with such modification of evaluating procedure as may be required for the particular test involved.

The committee members present and concurring in these recommendations are Messrs. Knowland, Hager, Durfee, O'Neil, Meili, Monego and Holst. Miss Nickerson and Mr. Morrison were unable to attend the meeting.

Respectfully submitted,
D. P. Knowland, *Chairman.*
W. A. Holst, *Secretary.*

CONDITIONING LABORATORY

FACILITIES for carrying on the research activities of the American Association of Textile Chemists and Colorists will be improved by the installation of a conditioning laboratory and equipment. This laboratory, which will be installed at Lowell Textile Institute, will permit physical tests and other work to be conducted under controlled atmospheric conditions. Decision to install the conditioning laboratory was reached at a recent meeting of the Council of the Association. At present the Association has five full-time research associates and assistants whose work is supplementing the voluntary services performed by technicians and laboratories on research-committee projects. Research currently being carried out by the A.A.T.C.C. is centered largely on the development of standard methods for testing the colorfastness and other properties of textiles and standard methods of chemical analysis as applied to the textile industry. Recently, the research associates and assistants of the Association at Lowell Textile Institute have been cooperating with Jeffersonville Quartermaster Depot on the development of test methods for water repellency to be embodied in a new specification for dyed and finished cotton duck.

Lapel buttons, bearing the seal of the association, may be purchased by members in good standing from the Secretary at $1.50 each.

SHRINKAGE CONTROL OF WOOL*

ALDEN D. NUTE

Calco Chemical Division, American Cyanamid Co.

THE problem of controlling the felting shrinkage of wool has interested scientists for a great many years, but it has been only in the last ten or fifteen years that any real active development work has been undertaken in this particular field of endeavor.

It may be well to mention here that in the case of wool there are two types of shrinkage to be considered, relaxation and felting. During the manufacture and processing of yarns and fabrics, tension is applied. The resulting stretch is removed upon treatment with cold water, followed by drying in the relaxed state. This relaxation, or London shrinkage, normally ranges from two up to fifteen per cent, depending on the type of fabric or yarn being handled.

On the other hand, when wool is laundered or washed, felting shrinkage occurs, one explanation being that the fibers tend to move toward the root end, more or less in the manner of the contraction of a helical spring.

As far as we know, the first successful non-shrink process to be applied commercially was the one designated as "Wet Chlorination." This method consists of a treatment of the wool with an acidified aqueous solution of sodium hypochlorite and is used in England, particularly in the treatment of woolen knitted underwear material. Various modifications of this process, not covered by patent, are probably in use, and are designed to produce a more uniform result with a minimum of damage to the fiber. One modification, which is covered by patent, is the Negafil process of Clayton & Edwards, which makes use of chlorine in aqueous solutions containing formic acid. In this country, the Hypol process has been used with success in the treatment of athletic socks.

In mentioning some of the latest processes for controlling the shrinkage of wool, it may be well to state that only a very few have been used successfully here in the United States, although mills in England have had somewhat better results.

The dry chlorination of wool was worked out by the Wool Industries Research Association. In this method the wool, having a moisture regain of eight per cent, is placed in an autoclave from which the air is evacuated, and into which chlorine gas is then admitted. The chlorination lasts about one hour, after which the material is removed to be given an anti-chlor treatment. This process is known by the trademark "Woolindras."

Alden D. Nute graduated from the Massachusetts Institute of Technology with a B.S. degree in Chemical Engineering. During his fifteen years' connection with the American Printing Company in Fall River, Massachusetts, he held in turn the positions of chemist, chief chemist, assistant superintendent, and director of research. For four years he acted as assistant superintendent of the Print Works Division of the Pacific Mills in Lawrence, Massachusetts. Five years ago he joined the Calco Chemical Division of the American Cyanamid Company where he is now technical representative in textiles, and in this capacity he is particularly active in the development and application of special resins to textiles.

The sulfuryl chloride or Dri Sol process specifies that air dry wool be steeped in a solution of sulfuryl chloride in an inert solvent, such as Stoddard's solvent. Special equipment is required and control is very difficult.

In the use of the enzyme method, Papein or a similar material is applied in a sodium bisulfite bath. The better the shrinkage control the greater is the loss in weight caused by the action of the enzyme.

The application of caustic potash in methylated spirits, a method perfected in Sydney, Australia, is known as the Freney-Lipson process.

Speakman and his co-workers at Leed's University developed a method using sodium sulfide or other inorganic reducing agents in mixtures of alcohols, followed by treatment with metallic salts.

Experimentation with organic hypochlorites in an inert solvent, led to the patent of Jackson, Reichart and Peakes, in 1929, but as far as is known, no commercial application of this process has been undertaken.

Tootal, Broadhurst and Lee have patented a method involving a treatment of the wool with caustic soda or potash in a mixture of butyl alcohol and Stoddard's solvent. Control is rather difficult, but the results are said to be quite satisfactory.

The bromine process, like the chlorination processes, is difficult to control and no known large scale commercial utilization of this method has been made up to the present time.

Another method for controlling the shrinkage of wool was made known in a German patent issued in 1941. In this case, chlor-sulfonic acid is the active ingredient which produces the excellent control which the authors claim.

Thioglycols and similar materials have shown some promise in controlling the shrinkage of wool, but considerable care in handling and special apparatus is required.

A recent patented process of Speakman and Barr at Leed's University treats wool in any form to the combined action of water vapor and the vapor of a volatile monomeric vinyl or vinylidene compound. It is stated that increases in weight up to 200 per cent are possible. It is hardly necessary to mention that special equipment is essential for this process.

One of the latest processes, U. S. Patent 2,329,622, makes use of a methylated methylol melamine to control the felting shrinkage of wool.

In the commercial utilization of any of these processes, with the exception of the last mentioned, exceedingly careful control together with special and costly apparatus is required, in order to prevent excessive damage to the fiber. In practically every instance, the shrinkage control obtained is due to a degradation of the fiber, with a subsequent loss in wool content.

In the case of the method involving the application of melamine resin, to control the felting shrinkage of wool, there are many details which are certain to be of interest to everyone.

In all the following remarks, the term resin is applied to a low reacted monomer, which is a resin forming material.

It may be said in passing that urea-formaldehyde resins have been tried for wool shrinkage control and found wanting, principally because of the lack of satisfactory control and the poor hand of the treated

* Presented at meeting, Rhode Island Section, October 27, 1944.

goods. Of the many melamine resins investigated over a period of years, only one type, the alkylated methylol melamines, appeared to be of interest for application to wool. Toward the end of an intensive development program, a methylated methylol melamine was developed which is unique in its properties and particularly in its action toward this fiber. The name given to this particular type of melamine compound is Lanaset.*

This product is a special type of methylated methylol melamine, having a solids content of approximately 80 per cent, a pH of 8.0 and is miscible with cold water in all proportions. One of its most important properties is its excellent stability to storage, which is in sharp contrast to the relatively poor storage properties of those urea formaldehyde resins which have been, and still are used for certain non-wool shrinkage control purposes.

Lanaset has been applied to wool in raw stock, skeins, slubbing, woven goods, knitted wear and felts. In each case, the method of impregnation and subsequent handling varies to a considerable degree, although woven goods and felts are handled in much the same equipment and under similar sets of conditions. Our most successful applications to date have been in the field of woven fabrics and most of this paper will be devoted to this important and diverse field.

In any discussion of the application of Lanaset to wool fabrics, we must keep constantly in mind several factors of extreme importance. Firstly, it is necessary to add approximately 10 per cent of Lanaset by weight to the cloth to obtain maximum shrinkage control and secondly, such an addition of resin must not alter the hand of the fabric to any great degree. A slight crispness is desirable in men's wear worsteds, whereas women's wear woolens must be soft and drape well. It is imperative that the resiliency of the fabric construction be maintained as otherwise the drape of the goods is adversely affected.

The melamine resin may be applied to goods either in the dry or wet state, although it is generally recommended to have the fabrics dried thoroughly before impregnating, as this method of operating will produce more uniform results. However, impregnating wet with Lanaset has proven satisfactory in large scale production, as is attested by the fact that 130,000 yards of 21½ oz. blanket lining fabric for the army was handled in this manner. Naturally, the purpose of impregnating wet is to save one drying operation, which in a woolen mill is of considerable importance.

* Lanaset is the trademarked name of a melamine resin produced and sold by the American Cyanamid Company and its several divisions.

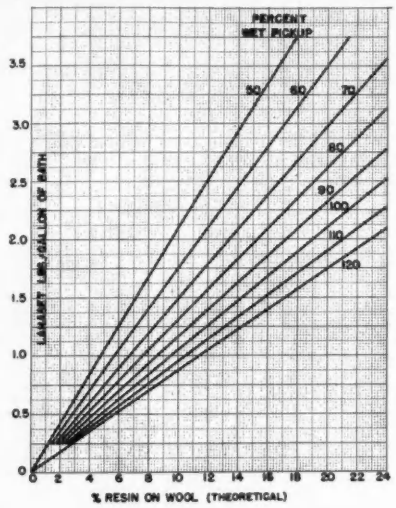


Fig. 1—Lanaset Bath vs. Per Cent Solids on Wool

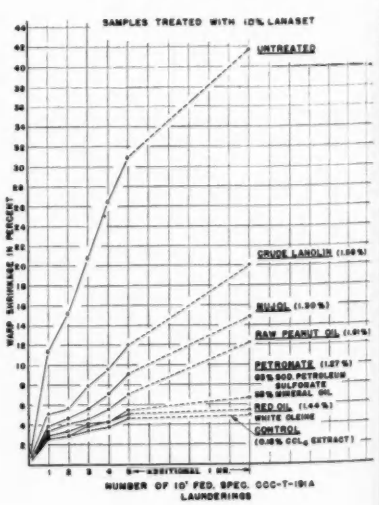
The most efficient method of applying the melamine resin to piece goods is to impregnate and dry in a single operation. For this purpose, it is necessary to have a pad mangle set up in front of a pin tenter dryer, so that the fabric after leaving the squeeze rollers of the mangle passes directly into the dryer. In some instances, due to lack of proper set-up of equipment, it has been necessary to pad and drop onto flat trucks, followed by a trucking of the goods to the dryer for the drying operation. This method of handling is open to several objections, chief of which is the extra handling involved. It is true, too, that where the Lanaset pickup is high, migration of resin may take place in the wet goods on standing, resulting in an uneven distribution of resin in the finished fabrics. This in turn means a variation in hand as well as in shrinkage control.

The best type of mangle for impregnating is one which yields a heavy set. An air pressure or an hydraulic mangle will give satisfactory results, particularly if there is a control attachment which will permit the pressure to be varied at will. For blanket constructions, which have been napped before impregnating, the pickup of Lanaset may be nearly 100 per cent, even with the hydraulic mangle. With such fabrics in an unnapped condition, the pickup is much lower, probably 60 to 70 per cent. In general, it is our belief that it is preferable to use a strong Lanaset bath with a low resin pickup, rather than a weak liquor with a high pickup. The advantages of such a method of application are that the resin is pressed into the fabric and fibers to a greater degree and the resulting hand of the goods is much softer. This is easy to understand, as the higher the pickup from the impregnating bath, the more the resin tends to be polymerized on the surface of the cloth during the subsequent curing operation, which of course results in a certain degree of harshness or boardiness.

While a 3 bowl mangle is a more flexible and useful unit, very satisfactory work has been produced on a 2 bowl mangle. In certain cases, either a wet out pad or a quetsch has been used for the resin impregnation, followed by a run through the hydraulic mangle to remove as much liquor as possible. However, this is not nearly as efficient as a single unit, consisting of the combination of heavy mangle and pin tenter frame. In the 2 bowl mangle, the rolls may be either both rubber or one rubber and one stainless steel, whereas in the 3 bowl machine, all 3 rolls may be rubber or the top and bottom rolls may be rubber, with a stainless roll in the center. A mangle box with a liquor capacity of 100 gallons is large enough for most purposes, but since the wet out time for different fabrics may vary between rather wide limits, it is best to have a box of several sections whose liquor capacity may be varied between 100 and 300 gallons. With a variable speed motor to drive this unit, the wet out time may be varied from a few seconds up to two minutes or more.

In order to obtain the best results with Lanaset, it is imperative that the oil content in the wool fiber be below one half of one per cent. Our maximum shrinkage control results to date have been obtained with goods having an oil content under one-quarter of one per cent. Investigations at the Stamford Laboratories of the American Cyanamid Company, indicate that different types of oils affect the action of Lanaset in varying degrees, particularly

Fig. 2—Effect of Oil Type on Shrinkage Control with Lanaset



when present in excess of one-half of one per cent. Spinning or other oils applied during the processing of the wool may normally be removed almost completely by either a scouring or dry-cleaning operation. This factor of removal of oil or grease from a fabric before resin application is of extreme importance and should be constantly borne in mind; otherwise, results will be erratic and discouraging.

A very important point, which is stressed by all mill men, is that the hand and feel of the fabric, as well as its ability to breathe (porosity) must not be changed to any great degree by any shrinkage control process. Lanaset alone, or in conjunction with a special class of softener developed specifically for use with this melamine type of resin, does maintain these properties to a marked degree. In sharp contrast, the chemical methods harshen the goods, as the structure of the fiber is changed by such treatment. In these cases there is a subsequent loss in weight, which may run as high as from five to ten per cent. Contrast this, if you will, with the five to fifteen per cent increase in weight due to the application of the melamine resin.

Of the many advantages offered by this resin process, the most striking are ease of application from a water system, no costly or complicated equipment required, and a continuous method of handling which does not necessitate particularly accurate or sensitive control.

For most fabrics, the hand, resiliency and wearing characteristics are practically unaffected by the application of the melamine resin. The abrasion resistance is usually increased, the tensile strength and moisture regain figures remain about normal, with the porosity or breathing ability unimpaired.

In conclusion, we may say that a remarkable stride forward has been made in the development of a resin method to control the felting shrinkage of wool. We realize, however, that considerable further effort is required to iron out the many and diverse problems connected with such a complex material as the wool fiber. The active cooperation of the woolen mills is needed and earnestly requested in order to insure a reasonable degree of success for this melamine resin process.

(The speaker then showed several tables. See Tables 1 and 2. These brought forth more explanations and elucidations. Also some pictures of fibers and fabrics before and after treatment, and the subsequent launderings. Several types of fabrics were also shown. Some of the comments on these follow.)

DISCUSSION

Q. At what stage in the wool operation is resin applied? I take it that it is done usually as the final finish. If it should not be done at that stage, what effect would it have on the dyeing properties?

A. That is very well shown in these samples. (Exhibiting them) In one case the yarn was treated with melamine resin (top of the piece shown); in the lower piece, the yarn had no treatment at all. Then the pieces were knitted and subjected to laundering. You will find that this piece which has had no treatment felts very badly in the laundering operation, whereas the lighter piece which has been resin-treated felts practically not at all. I think if those pieces are passed around, most of you can easily understand what goes on. That covers the application to yarns.

Now in regard to application to sliver or slubbing, in this case you have a sweater and the sliver or slubbing was treated with the melamine resin, following which the sweater was knitted. The other half of this lot of yarn was held out and knitted also at the same time, presumably on the same machine, and then these two sweaters were laundered at the same time under the same conditions. I think you will see that there is a considerable difference in those two sweaters. (One was badly felted)

Now, when it comes to piece goods, we have in one case a 10½ ounce tropical worsted which was treated in the piece with the melamine resin, and in another case the fabric was finished in the normal manner. Now these two suits represented by these two jackets (holding them up) have been worn all summer and have had six dry-cleanings. The principal advantage of the resin-finished suit is that it is cooler. It does not cling to the body during the hot weather. As one perspires, the resin-finished suit seems to hold away from the body whereas the regular finished suit clings badly. I do not think that the suits have been worn long enough to show too much variation up to the present time.

The wool felt in this hat received a little different application. It was treated with the resin in the form of a continuous length and then dried, cured and washed in the regular way before being made into this hat. The reason for using the process here was for shrinkage control. The normal felt that goes into this hat has a shrinkage of 10 per cent or more just by treatment with *cold* water, whereas the resin-treated felt has no shrinkage. That was a very important application for that particular type of felt.

As for applying the resin to raw stock, we find that the spinning and weaving operations are very apt to cause a loss in the shrinkage control effect—a very difficult thing to control. Up to the present time we have not been able to treat raw stock very successfully, though it may be possible to do so later, particularly if high-temperature curing is carried out. Curing at 300° F. or below does not seem to *maintain* the properties in raw stock that we may expect if the curing is carried out at 400° F. or higher, or at what we call FLASH curing. This FLASH curing gives a much harder resin and has a tendency also to cut down the relaxation shrinkage, which is very important to the spinners.

Q. What is the proper curing time?

A. That more or less depends upon the

Table 1—Effect of Temperature on the Tensile Strength of Wool

Treatment	Tensile Strength—3" grab (lbs.)			
	Cloth A		Cloth B	
	W.	F.	W.	F.
Wet out—Heated 5 minutes at 290° F.	54.9	60.3	46.3	30.3
Wet out—Heated 15 " at 290° F.	55.0	60.8	...	...
Wet out—Heated 30 " at 290° F.	53.9	61.5	46.5	30.0
Wet out—Heated 45 " at 290° F.	...	...	47.8	31.8
Wet out—Heated 60 " at 290° F.	55.3	59.0	...	...
Left dry—Heated 60 " at 290° F.	55.8	62.8	...	...
Wet out—Heated 9 " at 350° F.	...	...	45.3	34.8
Control—not heated	55.6	60.9	45.8	30.0

Cloth A—8.5 oz. plain weave suiting no nap Cloth B—8 oz. women's wear flannel

Table 2—Shrinkage Control Obtained on Mill Trials of Lanaset

Number of Launderings Given	Shrinkages* in Per Cent											
	Cloth 1				Cloth 2				Cloth 3			
	Untreated		Treated		Untreated		Treated		Untreated		Treated	
	W.	F.	W.	F.	W.	F.	W.	F.	W.	F.	W.	F.
1	2.5	0.5	2.0	0.3	18.3	15.2	4.2	4.7	4.0	1.5	2.5	1.3
3	4.3	1.7	2.8	0.5	22.0	18.7	5.9	5.2	6.5	3.5	3.5	2.0
5	6.3	3.2	3.9	0.5	..	..	..	..	8.5	5.8	4.5	2.5
7	8.7	5.5	4.6	1.1	..	..	..	..	..	..	..	..
10	10.3	8.4	5.0	0.9	..	..	..	..	13.0	10.5	5.2	2.5

*Samples given wool launderings 10′ at 100° F. according to Fed. Spec. CCC-T-191A.
Cloth 1 Tropical Worsted Cloth 2 Plaid Flannel Cloth 3 80% Wool, 20% Cotton Army Shirting

plant in which you are working. The cure can be as low as 230° F. but with a 10½ ounce tropical worsted a period of at least one hour at that temperature would be necessary for a complete cure. As the temperature goes up to 250° F., it will take 40 minutes; 280° F.—10 to 15 minutes; 300° F.—5 minutes; 350° F.—2 minutes; 400° F.—15 seconds. We have never tried curing above 400° F., but there is one plant operating at 400° F. with the actual time of 10 to 15 seconds. When we compared the results of this curing against that of a plant where the curing time was 40 minutes at 250° F., the shorter, hotter cure gave the better shrinkage control.

Q. As far as your work has gone, what would you consider the ideal condition for curing?

A. That depends more or less on the type of fabric which you are handling. I would say, roughly, two minutes at 350° F. for a tropical worsted. One and one-half minutes might be enough, but it would have to be checked for each fabric as processed. Generally two minutes with very good air circulation should give excellent shrinkage control. There is a point there which may be bothersome to some people; that is, just exactly what we mean by a *good shrinkage control*. Shrinkage control should never be 100 per cent perfect because when these garments are made the shoulders are always fitted by steaming; i.e., the tailor steams the goods in order to fit the garment properly, which, in the case of women's wear fabrics, is extremely important. If the shrinkage control were 100 per cent the garment would not fit properly at all so that the actual shrinkage should be controlled down to say 3 per cent in warp and 1 per cent in the filling if the fabric had a normal shrinkage of 10 per cent in warp and 6 per cent in filling. The 21½ ounce blanket lining fabric for the Army, in which the normal shrinkage was 10 per cent in both warp and filling, after a melamine resin treatment had a shrinkage of less than 5 per cent in warp and 2 per cent in the filling.

Q. Why wouldn't 100 per cent shrinkage control be satisfactory in the case of blankets?

A. In the case of blankets, it is very difficult to find out who knows what a properly shrunk blanket is. Today I talked with a gentleman at the Esmond Mills who has a friend in Washington, a good authority on this subject, and he said that *he* did not know and didn't know anyone who did know. He stated that he thought if we were able to control an all-wool blanket shrinkage by this treatment to 5 per cent in the warp and 5 per cent in the filling, he would consider that an excellent job. I would like to say this in regard to blankets: some blankets shrink very much differently than others. Some blanket fabrics after the usual processing, have a normal shrinkage of 25 per cent in the warp and 40 per cent in the filling after ten launderings, so it is almost impossible for one to try to control it. The shrinkage depends on the cloth and the amount of drying and stretching it was given in the plant.

Q. In regard to shrinkage control of blanket linings, are you referring to the relaxation shrinkage or felting shrinkage?

A. Felting shrinkage.

Q. Why does a fabric shrink more in warp than in filling? Is this general?

A. No, that is not true. It varies considerably. This particular fabric shrank more in warp than filling, but some act in the opposite manner, although most all that I have found have had more shrinkage in the warp than in the filling.

Q. Have you any answer as to why this is so?

A. It is largely due to the construction. Different methods of finishing and other variations in handling are also contributing factors. As an example, if a fabric of 58″ in width is finished to 56″, the final filling shrinkage is lowered as compared to finshing to 58″. So you see the method of handling is extremely important.

Q. Your charts indicate that there is no appreciable loss in tensile strength when the goods wet out with water are subjected to these high temperatures. What are the effects when wet with resin solution?

A. That is a very good question. We find that under proper conditions of handling there is practically no loss in tensile strength. Of course, there is always a question as to what is the proper method of handling: drying under proper conditions and curing under proper condition. Over-curing will give loss of tensile strength and under-curing will give a higher tensile figure.

Q. How does the Lanaset process compare with the chlorination method?

A. The chlorination method always harshens the wool and it seems to chemically destroy or change some of the wool scales. Therefore, there is always a loss in tensile strength and in weight. None of these defects are found when goods are properly processed with the melamine resin here described.

Q. Has any practical use been made of caustic soda to stop shrinkage?

A. Are you speaking of wool?

Q. Yes.

A. You may be thinking of the Freney-Lipson process with alcoholic caustic soda.

Q. No. This was an aqueous solution of about 53 per cent.

A. I do not think that there has been much practical use made of that in the last hundred years. I don't see how that would ever work.

Q. Do you attribute your results to the film-forming properties of the resins closing the scales of the fiber?

A. That probably is true. We also know that resin *does* penetrate the fiber. This resin treatment also gives some protection against alkali. If two pieces of fabric are taken, one of which has not been resin-treated and the other that has been resin-treated and a piece of each is dropped into a beaker of cold caustic soda solution (5 per cent), within a period of one or two hours the non-treated fabric has been disintegrated whereas the other maintains its construction.

Q. That should be of material value in printing of wool.

A. That probably is true. That is something we have had in mind but due to the war effort we have been spending our time on other things.

Q. What is the optimum resin content of a fabric?

A. This is rather a strange thing: when 10 pieces of blanket fabric, having been knitted with the same fiber and same yarn, sewn together end to end, put through the same resin bath, and the same washing and finishing operations, we found that the resin content will vary from 4½ to 5 per cent up to 7½ to 8 per cent. It is a little difficult to understand why this should be, but in order to eliminate any variation in final shrinkage control results, we recommend a resin bath strong enough so that we will still get a maximum control whatever variation there may be in the wool itself.

Q. Has this resin content been as high as 12 per cent as shown in the chart?

A. We have run as high as 15 per cent, but when there is 10 per cent resin on the fiber the results are just as good as when 15 per cent is used, provided it is fixed efficiently.

Q. Is a melamine resin treatment of *cotton* better than the urea-formaldehyde type?

A. We feel that melamine resin is much better. The particular reason for that is this—for one pound of melamine resin in a fabric you would require 2 pounds of urea-formaldehyde approximately. That figure is rough, but we have checked it in many cases. This reason, the relative bulk, is why melamine resin is more satisfactory on wool than urea-formaldehyde. If you had twice as much, or 20 per cent of urea-formaldehyde in place of 10 per cent

(Concluded on Page P176)

ARALAC*,†

DUNCAN G. CARMICHAEL

Aralac, Inc.

THIS paper tonight under the general heading of "Aralac" will be divided roughly into two parts. First we shall say something of the history, manufacture and properties of Aralac and later we shall discuss the processing and dyeing of various types of materials containing "Aralac."

ARALAC CASEIN FIBER

Casein fiber has been of considerable interest since Dr. Ferretti produced this type of fiber commercially in Italy in 1936.

Aralac, Inc., a subsidiary of National Dairy Products, after four years of experiments, announced a new casein fiber in 1940. Since then, it has increased its production eightfold.

The original 4,000 pounds-a-day plant of Bristol, Rhode Island, was moved to Taftville, Connecticut, in July 1941 with an output of 15,000 pounds per day. The success which this fiber has met in the textile trade has doubled the plant production so that this year 30,000 pounds is the daily output.

Casein fiber is made by a wet spinning process similar to viscose rayon. At one point only, however, are these two processes similar and that is the extrusion of the spinning solution through a spinnerette into a coagulating bath.

Previous to this point in the process, the Aralac process is much simpler than the viscose. Afterwards, it is many times more complicated.

The casein is dispersed in water by means of an alkali. The dispersion is then clarified, spun, coagulated, and the filaments treated in a hardening bath to give flexibility and hot water resistance. The type, number, and sequence of steps is varied and determined by what use is to be made of the finished fiber. The treatments serve to change the casein molecule into a new resin compound.

Aralac, for use in textiles, is subjected to Aralac's patented aratherming process. Aratherming is an acetylating process which gives the fiber improved stability. This stability is most outstanding when compared with other casein fibers.

The acetylation of casein fiber affects its chemical reactivity with chemical compounds. The fiber becomes resistant to boiling water and acids, and more resistant to alkaline solutions. Casein fibers, un-acetylated upon heating or boiling becomes soft, slippery and slimy in aqueous solutions, and upon drying decreases in tensile strength and becomes somewhat brittle. The effect is more pronounced with weak alkaline solutions, resulting in the disintegration of the fiber if the treatment is prolonged at high temperatures. When dyed in combination with natural protein fibers, un-acetylated casein fiber has a tendency to absorb all of the dyestuff, leaving the natural protein fibers undyed or stained.

The chemical properties of casein fiber are altered by acetylation to the extent that its dye absorption will approach natural protein fibers, so that both fibers, by selection of dyestuff will be dyed the same shade in the same bath.

Acetylation and other operations involved in the manufacture of Aralac are under a very thorough and rigid control and intensive mixing of batches insures complete uniformity.

Aralac, in its chemical constitution and many of its physical and chemical properties, has a great resemblance to wool.

The chemical composition approximates that of wool:

Element	*Aralac*	*Wool*
Carbon	53%	49.31%
Hydrogen	7.5%	7.57%
Oxygen	23%	23.66%
Nitrogen	15%	15.86%
Sulfur	0.7%	3.6 %
Phosphorus	0.8%	0.0 %

An X-ray examination of casein fiber shows the usual pair of rings, corresponding to the skeletal structure of the molecular chains present in natural keratin fibers.

These chains are not as regularly oriented as they are in wool, as confirmed by optical examination. In natural wool the reversible elastic properties are due to the coiling and uncoiling of its regularly arranged polypeptide chains.

The lesser degree of elasticity, as shown by casein fiber, arises from the partial uncoiling of the randomly oriented chains.

Aralac, under the microscope, presents a smooth fiber similar to rayon, but with a circular cross section. Being of a protein base, it burns with the same odor and bead formation as natural protein fibers.

The dry strength, elongation, and recovery after stress, compare favorably with wool. The plastic flow and elasticity are greater in the wet state than in the dry. Its strength, wet and dry, is about 30% and 75% respectively that of wool. Regain at 70°F and 65% relative humidity is 12.6%. Commercial regain is 13%.

Aralac possesses a most desirable feature in comparison with natural proteins in its uniformity which naturally results from a man-made fiber.

Aralac is offered in fineness corresponding approximately to 50's, 60's, and 70's wool grades, and in any staple length from ½" to 6".

Aralac is being used in cotton, rayon, and wool systems manufacturing all types of blends and fabrics of various construction.

The largest use of Aralac at present is in dress goods, but is expanding into other fabrics where a resilient lofty hand is desired.

The hat trade absorbs large quantities and approximately every felt hat in this country and Canada, which has been made within the last two years, contains some Aralac.

Specialty uses include filling for pillows, comfortables, and quilted goods, 100% Aralac interlinings for cool-weather garments, and protection for milady's hair when given a permanent wave. The last mentioned item is a highly crimped and combed top and is known under the trade-mark "Wavecrepe."

Fabrics containing Aralac fiber have been subjected to exhaustive tests, including resiliency, tensile strength, abrasion, odor, affinity to dyes, ability to withstand dry cleaning and washing, and have been found to be satisfactory to the textile trade.

Considerable research is being done and no doubt many improvements will develop in the future.

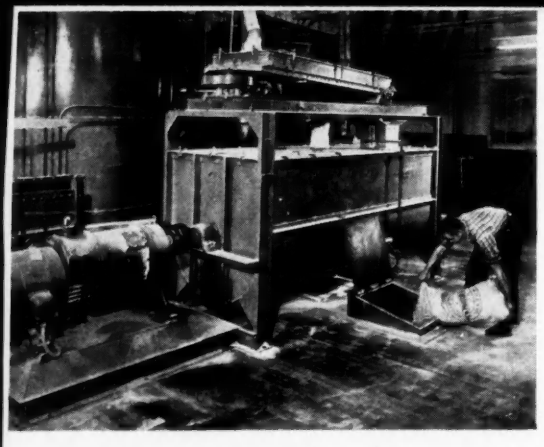
PROCESSING OF ARALAC AND SPUN RAYON FABRICS

In general, with some modification, Aralac will withstand the same wet treatments as natural protein fibers, with the exception of scouring in a highly alkaline bath, or other treatments that necessitate a high pH.

In fabrics containing a mixture of synthetic fibers, it becomes more than necessary for the dyer to make experimental dyeings before proceeding with the lot of mixed fiber goods.

* Presented at meeting, Rhode Island Section, September 29, 1944.

† "Aralac" is National Dairies' trade mark for protein fiber discussed in this article.



Note: All photos are through the courtesy of Aralac, Inc.

MIXING AND LIQUEFYING

Ground casein is poured into trap-door, thoroughly mixed in machine in foreground, treated with chemicals and heated in huge vats, left background.

The time, temperature, volume of dye liquor, and dyeing assistants should be carefully duplicated as to plant scale. This is advised, rather than trying to hurry through the dye lot by building the shade up in the dyeing and then encountering a lot of difficulty in the matching of the various fibers. It is sometimes quite difficult to determine the shade of the individual fibers in a mixed fiber fabric. Small skeins or samples of cloth containing the individual fibers attached to the dye lot will help in the processing.

Desizing.

Aralac and rayon, and Aralac and cotton fabrics should be desized in the same manner as similar all-spun rayon and cotton fabrics. There are a number of desizing agents on the market that have proved suitable for fabrics containing Aralac. The desizing agent may be padded or applied in a mangle and allowed to stand for a couple of hours or over night. The desizing may also take place in the jig or dyebeck. The method and product depends on the individual. Improper desizing may be responsible for trouble encountered later causing streaky, shaded dyeings, and affect the hand of the fabric in finishing.

Glue, gelatine, water soluble resins or easily solublized starches that have been satisfactory on wool fibers, should be used for sizing Aralac and Aralac combinations.

Tinting or Sighting Colors

Tinting or sighting colors for Aralac must wash out easily and should not stain acetate, rayon or wool in the scouring bath.

Aralac, being on the acid side, when in a desizing bath, has a tendency to pick up acid colors, which are usually used as tinting colors. Therefore, it is quite essential to use acid colors that are of the strong acid dyeing type and dye on protein fiber rather slowly. It is also possible to desize a fabric with an enzyme in a slightly alkaline bath, which would prevent the Aralac from absorbing the acid tinting colors. The following types have been found to come out satisfactorily in the usual dye-house processing, if not applied too heavily:

Fast Light Yellow 2 G (Colour Index #639)
Tartrazine (Colour Index #640)
Naphthol Yellow S (Colour Index #10)
Cochineal Red A (Colour Index #185)
Amido Naphthol Red G (Colour Index #31)
Amido Naphthol Red 6B (Colour Index #57)
Indigotine IA (Colour Index #1180)

Starches and ingredients of the sizing should be checked as to their binding properties in relation to tints. On filling yarn, care should be taken with the type of emulsions with which the sighting colors are applied. Some emulsions may have a tendency to hold the tints on drying, break on steaming (due to acidity of Aralac) or form insoluble bodies in the desizing operation due to the building up of acidity in the desizing bath. The tint set in any of the above ways would be difficult to remove in the regular scouring bath.

Oils or lubricants used with the tinting colors should emulsify directly in hot or cold water and should require no boiling with alkalies having a high pH for removal, and should not break easily with weak acid solutions.

When tints were first introduced they really were tints, but gradually deeper and deeper tinting has been relied on due to the increase in various twists, qualities and mixes, until pieces in the greige goods are actually heavy enough for dyed shades. Therefore, it is most important, regardless of what types of tints used, to apply them so that they are easily removed by the dyer without extra processing, such as stripping and reducing the tint. Tints should be applied only to a sufficient depth in order to distinguish from yarn not tinted.

Many difficulties, such as filling bars, warp streaks, and other defects may be traced to heavy tinting.

Scouring or Neutralizing

Aralac fiber as supplied to the trade at the present time is slightly acidic. The acidity is due to a small quantity of residual acetic acid left in the fiber from the acetylation. This acidity should be neutralized, otherwise, the Aralac fiber will absorb the dyestuff rapidly and quite heavily in combination with other fibers, even at low temperatures. At this stage Aralac may be compared with carbonized natural protein fibers. In neutralizing, low temperatures and short periods of time should be adhered to, depending on the type of material, weight and the weave of the cloth. Mild alkalies and synthetic detergents give the most satisfactory results. Only mild alkalies such as di-sodium phosphate, borax, sodium bicarbonate, or a smaller amount of sodium tetra pyrophosphate should be used. Ammonia, soda ash, alkaline soaps, sodium silicate, caustic soda or other chemical having a high pH should not be used in processing Aralac. About 0.7 per cent of residual acid is left in the fiber and 10 per cent of di-sodium phosphate on the weight of the Aralac has been found most satisfactory in neutralizing this residual acid.

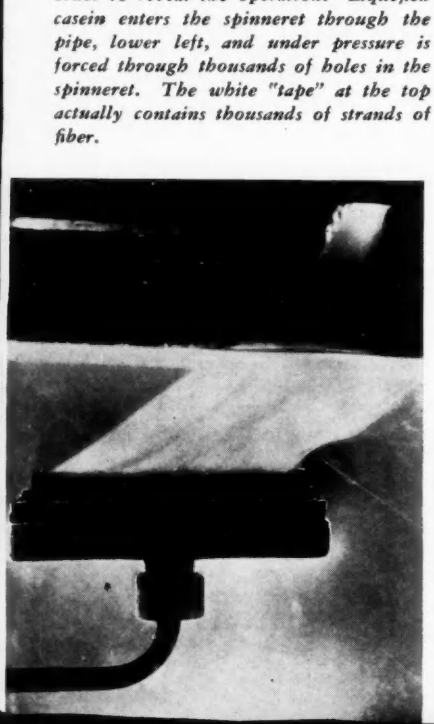
It is very essential to have the goods evenly neutralized, otherwise, uneven dyeing will be the result.

Dyeing

The behavior of Aralac towards direct dyestuff is similar to that of natural protein fibers. Aralac, when neutral, will remain practically unstained by wool white direct dyes, in a dyebath of a pH from 6.4 to 7. At a pH of less than 6.4 as the acidity increases, the absorption of

SPINNERET IN ACTION

This is an unretouched photograph of Aralac fiber as it comes out of the spinneret. This action was simulated in a specially prepared glass case using a more transparent solution than normally, in order to reveal the operation. Liquefied casein enters the spinneret through the pipe, lower left, and under pressure is forced through thousands of holes in the spinneret. The white "tape" at the top actually contains thousands of strands of fiber.



SPINNING BOX

Concealed under the foam are four spinnerets. Those four taffy-like strips are Aralac fibers in one of the first stages of processing. Hand indicates relative size. The fiber undergoes many other processes before it is ready for market.

he wool white direct colors becomes progressively higher. Aralac has a great affinity for acid dyestuffs, particularly the milling and neutral-dyeing dyestuffs.

After the neutralizing scour, the goods are dyed in a fresh neutral bath, with the addition of a neutral dyeing assistant, if necessary. Satisfactory results are obtained by using the direct wool white colors in a neutral bath for the cellulose fibers. This type of dyestuff, in light and medium shades, leaves the Aralac undyed or slightly stained, depending on the temperature. The Aralac is dyed with neutral-dyeing acid or milling colors. The Aralac in dark shades will require less neutral acid dyestuffs due to the Aralac staining heavier. The staining effect depends largely on the pH of the dyebath, as in the case when dyeing wool and rayon blends. Union colors can be used satisfactorily, depending on temperatures and combination of fibers.

Two-color effects can be obtained by careful manipulation.

The rayon can be left white by dyeing the Aralac with acid dyes that do not stain rayon.

Acid dyes exhaust well on Aralac so that only about ½ or ¼ of the amount of organic acid required for wool and rayon mixtures should be used. The Aralac may be reserved by dyeing the rayon with selected direct colors that leave wool white. The neutralized gods are dyed in a neutral bath using about 3 per cent of an auxiliary product that retards direct wool white dyestuff from dyeing on protein fibers. The material is run for ten or twenty minutes, then the selected wool white dyestuffs are added. The temperatures should not exceed 150 degrees F. and the usual addition of Glauber's Salt is made.

Dyeing Temperatures

Dyeing temperatures are best kept between 180 degrees—200 degrees F. The goods should not be boiled for any prolonged length of time as this has a harshening effect on Aralac.

Finishing

Aralac should have an acetic acid rinse after dyeing as this has been found to be quite advantageous to the final condition of the fiber, particularly before drying.

Cationic softeners and other products will give very good results depending on individual choice of hand desired.

A soft hand found satisfactory and applied in the final rinse after dyeing is as follows:

1-3 pts. Acetic acid per 100 gallons.

4-12 ozs. Cationic softener depending on hand desired.

The cationic softener used should be investigated as to its effect on the fastness and shade of the dyestuffs used.

It is also advantageous to have a slight amount of acetic acid in the quetch providing it is compatible with the other components in the finish. No alkaline softeners should be used.

OTHER TYPES OF DYESTUFFS ON ARALAC AND SPUN RAYON

Sulfur Colors

Sulfur colors can be applied by the bicarbonate process, but offer no particular advantage to fastness.

Naphthol Colors

Naphthol colors have found little application on wool, but spun rayon and Aralac blends offer greater possibilities with this class of dyestuffs. Careful control of pH and method of application should offer interesting developments.

Vat Colors

Vat colors, due to their high alkalinity, would cause alkali damage if carried out with the normal vat dyeing procedure.

Aralac and spun rayon fibers have been dyed by padding on the reduced color. The time factor is so small that the short contact with the alkaline solution causes no damage. Another method used is to pigment pad these dyestuffs and develop the padded material on the jig with a reducing bath buffered with sodium bicarbonate.

Thioindigo types of dyestuff applied in the same manner as applied to wool would offer less possibility of damaging the Aralac fibers.

Solubilized Vat Colors

The solubilized vat colors or sulfuric-esters of leuco vat dyestuff have pronounced affinity for Aralac and have good fastness properties. Spun rayon and Aralac fabrics padded with these colors have very good wash and light fastness.

The solubilized vat colors are applied in a padder with ½ oz. of sodium nitrate per gallon at 120°F and then developed on the jig with 3 oz. of sufuric acid per gallon in oxidizing bath at a temperature of 120°F to 160°F, according to the dyestuff used. The material is washed and neutralized with di-sodium phosphate and a synthetic detergent.

Considerable work has been done with the various fast types of dyestuffs on combinations of natural fibers with Aralac and synthetic fibers with Aralac, but due to restrictions brought on by the war production, plant trials and practical runs have been out of the question.

ARALAC AND WOOL MIXTURES

The scouring of Aralac and wool fibers should be carried out at low temperatures and when necessary to use soap, a neutral soap should be used with a mild alkali. The mild alkali is necessary to prevent the soap from breaking and depositing the fatty acid on the fibers. Aralac and wool mixtures will felt faster than the same wool construction itself. This should be emphasized here, as the finisher will get any finish required in the washer without fulling.

Acid Colors

The dyeing of wool and Aralac combinations with the ordinary level dyeing acid colors such as azo phloxine, fast light yellow and alizarine sapphire combinations yield good unions at a pH between 2.5 and 3.5. Above a pH of 3.5 the Aralac becomes deeper in shade as the pH increases. As the pH decreases below a pH of 2.5 the wool fibers in-

RECOVERING CHEMICALS

In this apparatus, resembling a huge washing machine, chemicals are recovered for re-use. At this stage, the "tow" is nearly ready for cutting into small lengths.

FINISHED FIBER

From the revolving drum at the top, cut and finished Aralac fiber drops down, ready to be baled and shipped to textile mills and other users.

crease in depth. The pH of 2.5 or 3.5 may be obtained with sulfuric, formic or combinations of acetic and sulfuric acids. Dyeings with formic acid in practical plant runs have given level and uniform shades on the two fibers.

The dyestuffs will exhaust on the Aralac, between the temperatures of 120°F and 200°F while the wool fibers will not reach their maximum depth until a temperature range between 200°F and 212°F is reached. From the start of the dyeing to the temperature of 180°F, the dyestuff will be absorbed heavier by the Aralac fibers. After a temperature of 200°F is reached, the wool fibers will absorb the dyestuff and within a short period, at a temperature between 200°F and 212°F, the two fibers will equalize in shade at a pH of 2.5 to 3.0.

The fastness to light of the level dyeing colors on Aralac approximates that of the wool fibers, but the fastness to washing is slightly inferior to that of wool.

Milling Colors and Neutral Dyeing Acid Colors

The milling colors and neutral dyeing acid colors have an excellent affinity for Aralac when dyed in a neutral bath. It was found that when dyeing Aralac and wool fibers in a neutral bath that some dyestuffs dyed the Aralac heavy and others dyed the wool fibers heavy.

The wash fastness of these colors in some cases was inferior, therefore, it was necessary to select dyestuffs that gave a good union on the two fibers and also good wash fastness.

The following colors and their prototypes, when dyed on Aralac, are as fast to a standard neutral soap wash as they are when dyed on wool:

Xylene Brilliant Cyanine 6B
Sulfonine Orange GS
Sulfonine Orange R
Xylene Milling Yellow S
Xylene Brilliant Cyanine G
Xylene Milling Blue 6G
Xylene Miling Black 2B
Alizarine Milling Blue SL Ex.
Brilliant Alizarine Milling Blue G
Sulfonine Red G
Sulfonine Red RS
Sulfonine Brown PR
Xylene Milling Yellow S
Sulfonine Blue 5R
Sulfonine Red 3B
Sulfonine Red B
Polar Red B Conc.
Polar Red 3B Conc.
Polar Red R Conc.
Polar Brilliant Blue GAW
Neutral Brown RX
Gycolan Black WAL Ex.
Sulphon Cyanine Black DN
Sulphon Cyanine Black BA New
Polar Yellow R Conc.
Cloth Fast Orange 2RN Ex.
Cloth Fast Red GR
Supranol Orange GSE
Cloth Fast Green G
Indocyanine 6B
Alphanol Brown BUA
Fullacine Brown R
Neutral Grey 6RD
Polar Orange GS Conc.
Benzyl Fast Blue GL
Azo Flavine RS
DuPont Anthraquinone Green GH
DuPont Milling Orange R
Pontacyl F. Brown GGS
DuPont Milling Red 3B Conc.
DuPont Milling Red R Conc.
Pontacyl Brill. Blue RR Conc.
Pontacyl Brill. Blue B Conc.
Pontacyl Wool Blue GL Conc.
Pontacyl F. Blue GB Ex.
Pontacyl F Blue GBB Ex. Conc.

Chrome Colors

It was found that a number of the chrome colors did not give a satisfactory union on Aralac and wool. Some colors dyed the Aralac heavy, others the wool heavy. The pH of the dyebath and the casein-aluminum complex are governing factors of the variation in shade difference and the depth of shade between the two fibers. Chrome colors that show less variation in shade between the aluminum lake and the chromium lake should be used.

The top chrome method using a pH between 2.5 and 3.5 as used with the acid colors gave the most satisfactory unions. The lesser shade difference was noted between the two fibers when sulfuric acid was used at the above pH, but formic acid gave satisfactory results, with level shades.

Dyeing procedure with an approximate pH of 3.0:

Use 10 per cent Glauber's Salt
3 per cent Formic Acid
Exhaust with 2 per cent formic acid

Develop with the usual quantity of bichromate; the dyeing to be carried out at a moderate boil. In prolonged boiling, there is a tendency for the shade on the Aralac to become heavier than on wool.

The depth of the shade of Aralac may be increased by allowing the temperature to drop and shading with metallized dyestuff. Aralac dyes much heavier than wool with this class of dyestuffs, regardless of the pH. The metallized dyestuffs offer the same fastness on Aralac as they do on wool.

The following is a list of colors which dye Aralac and wool uniformly and which have fastness to washing and fulling when dyed by the top chrome method:

Diamond Flavine (Colour Index 110)
Chrome F. Orange 3RLA
Monochrome Red FGA
Diamond F. Red F. (Colour Index 419)
Monochrome Violet FBA
Acid Alizarine Violet N (Colour Index 169)
Acid Chrome Blue 3G
Fast Mordant Blue B
Sulphon Cyamine 5R Ex. (Colour Index 289)
Diamond Black PV (Colour Index 170)
Alizarine Cyanine GHN Ex. (Colour Index 1078)
Diamond Green SS (Colour Index 302)
Chrome Brown RO
Acid Anthracene Brown KE
Anthracene Indigo Blue NWN
Diamond Black F. (Colour Index 299)
Alizarene F. Grey BBLW
Eriochrome Blue Black R (Colour Index 202)

Chrome colors applied by the monochrome mordant method, with few exceptions do not produce uniform shades. The monochrome colors that dye uniformly are of an insufficient range.

ARALAC AND ACETATE BLENDS

Aralac and acetate mixtures can be dyed with any number of acetate colors. The Aralac usually dyes slightly lighter and flatter than the acetate fiber. Shading the Aralac with bright milling colors will give solid shades. Unfortunately, most of the acetate dyestuffs on Aralac are not fast to washing. A two-bath method using fast to washing milling or metallized dyestuffs on Aralac would be necessary to obtain satisfactory wash fastness.

The acetate and Aralac fibers are dyed with acetate colors. The Aralac is then stripped in a stripping bath until the Aralac is clean or lightly tinted. The Aralac fibers are then dyed in a fresh bath with metallized dyestuff. This is a costly and impractical method of obtaining fast shades.

ARALAC AND NYLON BLENDS

The level dyeing acid colors produce

good unions and bright shades particularly with formic acid with a pH between 3.0-3.5. The chrome colors may be used when wash fastness is necessary as well as the selected milling colors used for obtaining wash fastness on wool and Aralac combinations.

This combination of fibers looks very interesting, and many other post-war developments containing Aralac in combination with other fibers are still in the experimental stage.

DISCUSSION

All questions answered by Mr. Carmichael.

Mr. Carmichael: The question is often asked, why Aralac is not sold as a neutralized fiber. Neutralizing would be difficult to do in a continuous process or after the fiber is made. As a matter of fact, we consider the slight acidity a factor of safety: It might help to counteract alkali if used in excess in subsequent processing. In any case, neutralizing with alkali in the scouring or boil-off bath offers less trouble than doing it during the manufacturing of the fiber. The acidity is about the same as in carbonized wool.

Q. Does the pH vary from batch to batch?

A. Each batch is tested as made, and the pH does not vary more than 0.1 per cent. Even this slight variation is less on an average, as the batches are blended 20,000 lbs. at one time. The washing out of the acid is a slow process similar to a dialyzing action. Our blended fiber is more uniform than any natural protein fiber. The variations are lower and rather small and inconsequential compared with the pH of the neutralizing alkali.

Q. You mention the use of a mild alkali. What should its pH be?

A. About 9.5 as an upper limit. As neutral soap has a pH of about 10 before use, it should be buffered with a milder alkali such as di-sodium phosphate, borax, sodium bicarbonate or sodium tetra-pyrophosphate.

Q. In mixtures of wool and Aralac which are run to obtain a certain shrinkage, can one use the conventional fulling?

A. No. Run through a soap without alkali, then a washer.

Q. Has acid fulling, which would avoid the alkali question, been tried?

A. We have conducted no experiments nor have we heard of any plant runs.

Q. Would chlorination be one method of shrinkage control?

A. At present we use resins, not chlorination. A reaction occurs with chlorination, leaving the Aralac yellowish and brittle with lower tensile strength, without lowering the shrinkage, materially. Another approach involves the use of an enzyme such as papain, but this process has not shown interesting results. Resins, especially the melamine type, are very good, and less harsh than the TBL resins. Methyl methacrylate resins have possibilities but are still restricted by the WPB.

Q. Since Aralac has a lower sulfur content than wool, and we know that the sulfur linkages in wool have a great deal to do with that fiber's tensile strength, and also that a superficial treatment with caustic increases its tensile strength, what can you say about the chemical sulfur in Aralac?

A. Aralac has no di-sulfide linkages as in wool, rather the linkages are due to methylene groups, also aluminum bridges. It has been suggested that the action of formaldehyde joins up two amino groups with loss of water to form a methylene link, therefore, the tensile strength is due to entirely different factors in the structure. The only sulfur in casein is in the amino acid methionine.

Q. What research is being done to increase the tensile strength?

A. Although Aralac approximates the tensile strength of wool, fibers have been made with a much higher tensile strength which are being studied at the present time. Such fibers are shiny, not unlike rayon and it is questionable whether that is preferable to the soft, lustrous form in which it is now made and sold. By improved chemical and mechanical methods, fibers have been obtained with better strengths both wet and dry. The strength of the fibers has been improved since the first Aralac was marketed.

Q. Has stretching after spinning (as in making nylon) been tried?

A. Yes, but with Aralac the coagulation is slow and the method involves many difficulties.

Q. Has anything been done about the high water absorption?

A. Other casein materials are steeped in formaldehyde solutions, sometimes for three or four months (in the case of buttons), to make a water-resistant plastic. But then, when you consider the extreme fineness of the fibers in comparison with other formaldehyde hardened casein plastics and the large surfaces involved, you must admit the water would penetrate more quickly.

European methods involving the use of formaldehyde, have been such that the finished product will withstand boiling in water. We depend mainly on the acetylation to lower the water inhibition.

Q. Has anyone obtained real white Aralac?

A. The peroxide manufacturers have studied that problem extensively but to the present time have concluded that Aralac cannot be bleached as white as cotton without damage. In this respect, it does not differ from other protein fibers.

Q. Is there any way to improve the yellowish tinge?

A. By bluing, of course, but a dead white is obtained with a greyish tone. In cotton mixtures, with the usual motes and impurities of cotton, it is possible to kier boil with a mild alkali in an open kier, then peroxide bleach, and finally tint. Although the white is not as good as the usual bleach obtained on cotton goods, it is suitable for printing white grounds and dyeing pastel shades.

Q. What percentage of Aralac is used in blends?

A. With wool, up to 50 per cent; with acetate, 40 per cent; with viscose, 50 per cent; and recently some fabrics have been made with 70 per cent Aralac and 30 per cent viscose. 100 per cent Aralac fabrics are used as interlinings in fur coats and other expensive coats. They have the same warmth as wool and less weight.

Q. Will you please describe that dusting effect?

A. Dusting can be seen by rubbing the suspected or damaged fabrics between the hands and letting the dust fall on white paper for examination. Dusting can also be seen in certain spun rayon, viscose, and acetate fabrics, so it is not a characteristic of Aralac. Alkali damage can cause dusting of any protein fiber.

Q. Can Aralac be drycleaned?

A. No damage has ever been reported when drycleaning with commercial solvents. In fact, the acetylating process is done in a solution of such solvents. In washing Aralac, the usual precautions taken with wool apply: i.e. use of Lux or other mild soap in luke-warm solution and thorough rinsing, perhaps followed by an acetic acid rinse to improve the hand.

Q. Has Aralac been extruded in colored form?

A. Yes, black fiber has been produced and carbon black was the color used. But this has certain disadvantages; it soils the equipment and is only practical where large batches are required. Perhaps in the future, pigment colors may be used for the automobile trade where large batches of one color are required. Organic pigments can be used such as the very fast Monastral Blues, the Lithol Reds, Hansa Yellows, etc. For the present, the conventional dye methods are preferred.

Q. Do the pigments effect the tensile strength?

A. Yes, usually the coarse ones such as, titanium dioxide, barium sulfate, etc., definitely lower the tensile strength. Aralac pigmented with titanium oxide does not look delustered and only the microscope would show pigmentation to any extent.

Q. Is there not an optimum particle size for such pigments?

A. Yes, it is in the vicinity of one micron. When larger, say 10 microns, spinning troubles begin, because the holes in the spinnerettes become clogged.

Q. If one gets a portion of piece goods which might contain Aralac, how do you test for it?

A. Immerse in a 1 per cent solution of Eriochrome Azurole (C.I. 720) with 1 per cent acetic acid and boil for one minute. The Aralac will be dyed blue and the wool is stained a tan. This is also useful in microscopic examination of wool and Aralac mixtures for fiber content count. So far, we have not been successful with any chemical means of separating these two fibers quantitatively. Some work has been done involving the testing or determination of the phosphorus content in Aralac, but the latter is so small that results are not accurate and therefore doubtful. The usual method is to determine the relative amount of wool and Aralac by microscopic count.

Q. In a fabric consisting of 80 per cent wool and 20 per cent Aralac, which is fulled, dyed and finished according to quartermaster specifications, would the depth of the blue which is usually 20 per cent on the all-wool fabric show up as 18 per cent or as 22 per cent?

A. We have had no experience with, nor record of such a type of cloth.

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Shrinkage Control—

(Concluded from Page P170)

of melamine resin, you would have a very heavy fabric.

Q. Why should the melamine resin create a more substantial shrinkage in wool than in cotton?

A. I would not say that it does, particularly, except that in the case of wool melamine resin has a much better action. It probably is due to the combination of the resin and the wool. In that connection, we have tried to determine the amount of resin in a wool fabric but were not able to determine it. If we try to remove all the wool with caustic, some of the resin is removed, too. A nitrogen determination does not give the answer either, as both substances contain nitrogen.

Q. With this resin treatment, do you mean that you can launder repeatedly and have a fairly non-shrinkable condition; i.e., only 3 to 5 per cent of the original fabric?

A. Yes, that is true. The only thing with socks is that most of the hosiery plants have boarding machines that operate at a temperature of roughly 180° F. to 200° F. and there is no way of curing in these hosiery plants, but if we take all-wool socks and treat them in a laboratory, we can make them so that they are practically shrink-proof. There would be very little shrinkage during repeated launderings.

Q. Has it been tested for dermatitis?

A. That has been checked thoroughly by a competent dermatologist. We have a consulting dermatologist to test these various materials of ours.

In the case of socks, the Army has had 1000 tests made and in no case has dermatitis occurred. So I think that clears us very well.

Q. Isn't the patch test usually applied?

A. Yes. The way they normally clear is to have a fabric that has been melamine resin finished and one that might be finished with starches or gum worn by 200 subjects at a time; i.e., a patch of regular finish in one set and resin in the other set. If out of 200 people only two have dermatitis with the regular finish and two with the resin finish, then it is concluded that there is no more chance of dermatitis with one finish than there is with the other. In this particular instance, we have had 1000 people tested by patch test and we have also had 1000 boys wearing the socks in service without injury, so its harmlessness is proved conclusively.

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FLAMMABILITY OF CONSUMER TEXTILES

BECAUSE of the fire hazard involved in the use of certain types of consumer textiles and recent legislation governing the manufacture and sale of textiles which are flammable, the American Association of Textile Chemists & Colorists has, at the request of the National Retail Dry Goods Association, formed a committee to investigate current fire-hazard laws and to develop a flammability test for consumer textiles. Members of the committee are: F. Bonnet, American Viscose Corp.; H. E. Hager, General Dyestuff Corp.; Charles W. Dorn, J. C. Penney Co.; Edward Young, Princeton Knitting Mills, Inc.; Charles L. Simon, Industrial By-Product & Research Co.; Cameron A. Baker, United States Testing Co.; and H. E. Wilde, Merck & Co., Inc. At a meeting of the committee held March 27, in New York, various test methods were discussed, and specifications for a suitable test apparatus were tentatively agreed upon. Apparatus of this type is now under construction for use in several laboratories which are co-operating in the study.

A law enacted in California reads in part: "It is unlawful to manufacture, sell or offer for sale in this State any article of wearing apparel, cloth, drapery or other fabric or material, made from or containing any synthetic fiber which is wholly or in part made from or contains any hazardous, explosive or other substance in sufficient quantity so as to make such fabric or material more highly inflammable than cotton cloth in its natural state."

A revision of this law introduced on March 9, by Joe R. Yockers, California State Fire Marshall, states in part: "It shall be unlawful to manufacture, sell or offer for sale in this State any of the following:

"Any garment or wearing apparel made from or containing any cellulose nitrate product.

"Any garment or wearing apparel made from a fabric or textile that will flash, ignite or blaze within one minute when placed one inch over an electrical element that is adjusted to generate a temperature of four hundred degrees (400°) Fahrenheit at a point one inch above the element.

"Any garment or wearing apparel made from synthetic fabrics or textiles and having a pile or brushed surface unless such fabrics or textiles have been treated with an effective flame retardant solution and are plainly marked with a warning label indicating the flammable nature of the fabric, the fact that the garment has been treated with a flame-retardant chemical and the minimum life of the flame retardant treatment when subjected to laundering and cleaning.

"Any dolls, stuffed animals or similar articles made from or containing any of the materials or substances mentioned above which might be easily ignited and thereby contribute to the bodily injury of a child."

The object of the A.A.T.C.C. committee will be to develop a test method for the evaluation of comparative fire hazards of various textile materials for consumer use in a manner more sound and scientific than that outlined in the proposed revision of the California Bill. The term "more highly inflammable than cotton cloth in its natural state" further complicates the work of this committee. Cotton in its natural state can assume many forms in textiles. For instance, there can be no comparison made between the rate of burning of a heavy duck material to that of a light-weight cotton flannel. Again, many cotton fabrics will ignite, but probably not flash or blaze within the specified time, since the ignition takes place in the form of smoldering of the fabric. Such smoldering will sometimes consume the entire specimen. The problem, therefore, appears to be to devise a method of evaluating comparative samples of cotton and other textile materials.

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CALENDAR OF COMING EVENTS

Meeting, Rhode Island Section, Providence Engineering Society Hall, 195 Angell St., Providence, R. I., April 27, 1945. Speakers: Arthur McLean, Director of Application Laboratories, Aridye Corp., "Pigment Printing and Dyeing, Past-Present-Future"; Wallace Heintz, Organic Chemicals Dept., E. I. duPont de Nemours & Co., Inc., "New Lubricants for Oiling and Wet Finishing Woolens and Worsteds."

Meeting, South Central Section, Patten Hotel, Chattanooga, Tenn., April 28, 1945. Speakers: Clyde J. Horne, Dixie Mercerizing Co., "Hash"; C. A. French, Industrial Heat Engineering Co., "Uses of Infra-Red Rays as Applied to Textile Drying."

Meeting, Mid-West Section, Bismark Hotel, Chicago, Ill., May 5, 1945. Afternoon session: Dr. D. H. Powers, Monsanto Chemical Co., "New Developments in Textile Finishing"; "Information Forum"; Evening Session: Business Meeting.

Meeting, New York Section, Downtown Athletic Club N. Y. C., May 18, 1945. Symposium on "Correlation of Test Methods with Consumer End Uses." Annual Business Meeting.

Meeting, Northern New England Section, May 25, 1945.

Meetings, Council and Research Committee, New York City, June 22, 1945. Chairman of Sub-Committees, who wish to hold meetings on June 21, should notify Dr. Louis A. Olney.

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OTHER ASSOCIATION MEETINGS

Meeting, Amer. Assn. of Textile Technologists-Builders' Club, New York City, May 2, 1945.

Medal Meeting, Am. Inst. of Chemists, Columbus, Ohio, May 11, 1945.

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CONTINUING THE NEW ERA

THE passing of Franklin D. Roosevelt does not mark the end of an era. The President initiated an era. He died in the bare beginnings of it. On how well those beginnings are continued and moved ultimately to their conclusion depends the peace, the real peace—not of the world as a geographical globe—but of each man as an individual.

The motivating purpose of Franklin Roosevelt was to edit the more evil implications inherent in the phrase "Survival of the fittest." His concern was with the man who always ran third in the race. He abhorred the oppressor, and fought him, domestically as well as internationally. He regulated the strong at home, to give better opportunity to the weak. He raised the weak by direct assistance. He put a comma after "Survival of the fittest," and added, "so long as the weak are not harmed."

Call it political philosophy, economics, religion, whatever—it is the hope of the world: that no man progress at the expense of another.

Franklin Roosevelt strode out in this new direction. Dismiss, if you must, his methods. His objective was and is clear. He visualized a country, and a world, with the elevation of the individual paramount.

This is the yardstick for measuring our growth, or our stagnation and decline, from here on. Franklin Roosevelt believed the job could be done. He began it. He died working at it.

It is symbolic that Franklin Roosevelt died at the climactic hour of Nazi Germany's defeat—a Germany standing against those things for the individual man that Franklin Roosevelt stood for. Might again was not right. "Survival of the fittest" is a slogan for animals. The most abhorrent example of the old era goes down as the standard of the new era is passed on by its initiator.

How well are we going to carry it?

* * *

Note: We feel that the above comments by Ernest J. Finan, as published in "Knit Goods Weekly," are well worth reprinting here.

THE WATER REPELLENCY OF TEXTILE FABRICS

HELMUT WAKEHAM, WINSTON B. STRICKLAND, and EVALD L. SKAU

Southern Regional Research Laboratory[1]
New Orleans, Louisiana

The resistance of a fabric to penetration by water depends not only on the twist of the yarn and the closeness of weave, but also on whether the surface is easy or hard to wet. Wettability depends upon the chemical and physical properties of the fibers and those of the substances with which the fibers are contaminated or with which the yarns or fabric are finished. From a consideration of the physico-chemical principles of wetting, the contact angle between the water and the fabric is found to be of great significance with regard to water-repellent behavior of the fabric. The tensiometric test for determining contact angle permits an evaluation of the fabric finish independently of the weave construction. The contact angles determined on a number of samples correlated well with the usual spray-test ratings and with hydrostatic pressure and Gurley Densometer air permeability values when these were compared in the light of the properties they measure and of the characteristics of the fabrics tested.

TECHNICAL discussions of water repellency in fabrics have recognized two aspects of the problem: the water repellency of the fiber and yarn surfaces, and the waterproofness of the fabric (8, 14). The water repellency of fibers and yarns depends upon their own chemical and physical properties and those of the substances with which they are contaminated or finished. The waterproofness of the fabric, or its resistance to penetration by water, is dependent upon fabric construction (9, 10, 16), as well as upon the water repellency of the fibers. Wenzel (14) pointed out in this connection that the water repellency of a textile fabric involves phenomena similar to those observed in capillary tubes, and discussed the application of the contact angle concept and other fundamental principles of wetting to the design of better water-repellent materials.

The fundamental principles underlying the problem should be given consideration in evaluating the tests commonly used for rating the efficiency of water-repellent fabrics, namely, the well known spray rating and hydrostatic pressure tests now accepted by the American Association of Textile Chemists and Colorists as tentative methods for determination of water resistance of fabrics (17). The purpose of this article is to re-analyze the factors involved in water repellency, to present a new tensiometric test for surface wettability applicable to water-repellent fabric, and to compare the new test with the usual tests for determining the water resistance of fabrics.

THEORETICAL ASPECTS OF WATER REPELLENCY

The physico-chemical principles underlying wetting action (1, 6, 7), which have been shown to be of basic importance in any study of water-repellent textiles (14), may be enumerated as follows:

1. The ease with which a given liquid will wet a given solid is evaluated in terms of the adhesion between the solid and the liquid. This adhesion, W, has been defined (2) by the equation

$$W = \gamma (1 + \cos \Theta) \qquad (1)$$

where γ is the liquid to air surface tension and Θ is the angle of contact between the solid and the liquid. (The W in this equation should not be confused with the "adhesion tension" which is frequently used to evaluate wettability and which is equal to $W - \gamma$ or, by the equation above, to $\gamma \cos \Theta$.) The relation of these quantities is shown in the customary force diagram in Figure 1.

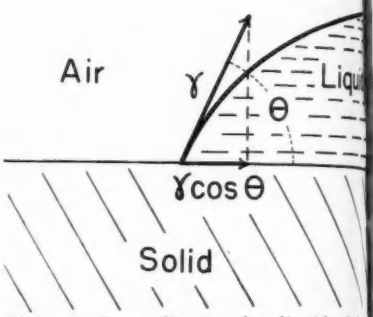


Figure 1. Force diagram for liquid-solid-air interface.

2. From Eq. 1 it follows that for a given value of the surface tension, γ, the adhesion, or the wettability of a given solid, is a function of the contact angle, Θ; thus, for small values of Θ, W is large and the solid is more readily wet by the liquid than when Θ is large. The contact angle, therefore, has an important bearing upon the water repellency or wettability of a surface, and in this respect has received recognition in both the paper and textile industries (3, 4, 5, 14).

3. The magnitude of the contact angle is determined primarily by the nature of the liquid and of the solid with which it is in contact. If the liquid contains some dissolved substance which will be adsorbed on the solid to form a new surface, the contact angle may be affected accordingly. Coating the surface of the solid with another substance may also change the contact angle. Finally, the contact angle, as ordinarily observed, is a function of the roughness of the surface; the smoother the surface the lower the contact angle for angles greater than 90° (15).

4. The motion of the liquid surface that comes in contact with a capillary tube depends largely upon the size of the capillary and upon the angle of contact between the liquid and the wall of the tube (See Figure 2). If the contact angle at equilibrium is small (less than 90°), the liquid will tend to move into and through the tube until the movement is opposed by an outside force, such as gravity, or until the surface forces causing the motion are changed due to changes in the nature or shape of the solid and liquid surfaces. If, on the other hand, the contact angle is large, the surface forces acting on the liquid will be exerted in such a direction that they tend to oppose this motion, and pressure must be applied to force the liquid into the tube.

A porous fabric is full of small capillaries. The fibers lying side by side in the twisted yarn form very narrow spiral openings, or microchannels, which can be

[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

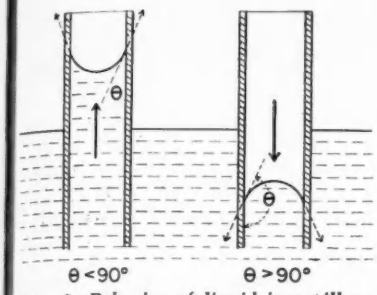


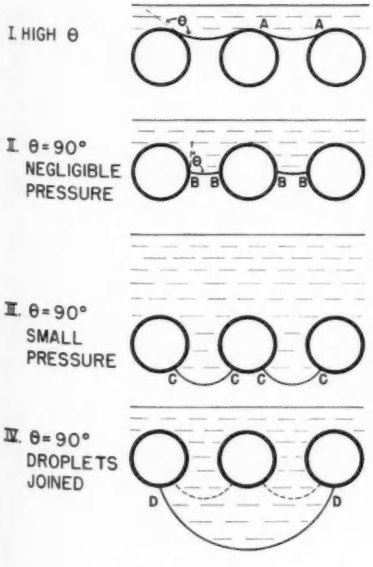
Figure 2. Behavior of liquid in capillary tubes.

clearly seen only with some magnification. The weaving of yarns into cloth introduces larger openings, or macrochannels, which tend to run through the cloth perpendicular to its surface. Both these types of openings are functions of the fabric construction, that is, of the tightness of the twist in the yarn, the type and closeness of the weave, and the weight of the fabric.

If the contact angle between the fabric material and water is low, any water placed on the surface of the cloth will wet it and move through both the macro- and microchannels until the fabric is penetrated. Treating the capillary walls (or the fibers) so that the contact angle is high will prevent this capillary action, especially in the microchannels. But water placed on the fabric surface will penetrate the macrochannels to some extent even if it does not wet the fibers. The depth of this penetration depends upon a number of factors which will be discussed briefly.

Suppose the cross section of a set of parallel yarns in a fabric is schematically represented by the circles in Figure 3. If the contact angle is larger than 90°, the equilibrium position of the water level will be something like the line AA in I. The degree of penetration by the water will be very low and, unless the water is forced into the openings under considerable pressure, the fabric will be fairly efficient as a water-repellent material.

Figure 3. Penetration of macrochannels by water as affected by contact angle and pressure.



If the contact angle is 90°, the equilibrium position of the water level will not be reached until the water is already partially through the opening as represented by the lines BB in II. This is due to the shape of the opening and to the tendency of the water surface to assume its characteristic contact angle and spherical shape. A small pressure will force the water through to form drops (represented by the lines CC in III) on the dry side of the fabric. Even in this state the surface forces are acting at the meniscus to resist the passage of the water through the cloth. But suppose this equilibrium state is disturbed by some means so that the drops are joined together as represented by the line DD in IV. The menisci of the individual drops are now lost and surface forces can no longer prevent movement of water through the cloth. When this phenomenon takes place the passage of the water is no longer affected by the contact angle between the fabric and the water. Once a fabric is wet through in this fashion, it makes little difference whether the treatment given the fibers was good or poor. The common experience of rubbing the inside of a tent during a rainstorm to obtain a trickle of water is an illustration of this phenomenon.

The pressure required to force the water through a small round capillary tube in which the contact angle is high may be calculated as follows: (Similar calculations may be made for square or rectangular channels with results that may be reduced essentially to those obtained below.) The force restraining the movement of water through the channel is exerted at the point of contact between the water-air interface and the solid, that is, at the circumference of the water meniscus.(See Figure 4.) The component of this force acting parallel to the long axis of the tube for each unit of circumferential distance is $\gamma \cos (180 - \Theta)$. Multiplying this by the circumference gives the total retarding force of $2\pi r\gamma\cos (180 - \Theta)$ for a tube of radius r. At equilibrium this will be opposed by an equal hydrostatic force which in this case is $\pi r^2 P$, where P is the pressure in appropriate units. Equating these forces and solving for P we have

$$2\pi r\gamma\cos (180 - \Theta) = \pi r^2 P, \text{ and, since}$$
$$\cos (180 - \Theta) = -\cos \Theta,$$
$$P = \frac{-2\pi r\gamma\cos \Theta}{\pi r^2} = \frac{-2\gamma\cos \Theta}{r}$$

Thus, the pressure required to force the water through varies directly as the surface tension and the cosine of the contact angle, and inversely as the radius of the channel.

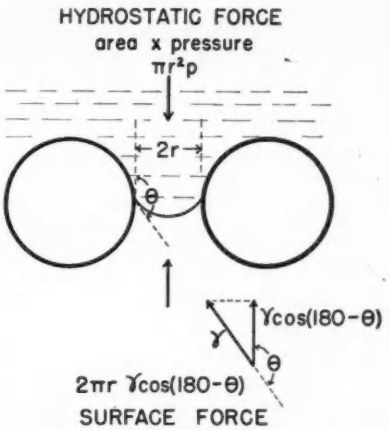


Figure 4. Relationship between hydrostatic force and contact angle.

A sample calculation will serve to illustrate the magnitude of the factors involved in this equation. If we use the values

$\gamma = 72$ dynes per cm. (for water at 25° C.)

$\Theta = 120°$, $\cos \Theta = -0.5$

and $r = 0.01$ cm.

then $P = \dfrac{2 \times 72 \times 0.5}{0.01} = 7200$ dynes per square centimeter

= 7.2 centimeters of water pressure (approx.).

Although this calculation was for the ideal case of a straight tube of uniform bore it gives a result that is in the range of hydrostatic pressure test values obtained on real fabrics.

This equation emphasizes the two requirements of a water-repellent fabric: (1) a fabric treatment to give a high contact angle, and (2) a fabric construction designed to reduce the size of the channels to a minimum.

We have yet to consider the effect of the impact of a drop of water upon a water-repellent fabric. The force or pressure exerted when a drop strikes a fabric surface may be estimated on the basis of a few simple assumptions. If the water is dropped from a height of 24 inches, as in the impact penetration test (10), it will have a velocity of approximately 340 centimeters per second when it reaches the fabric.

Assume:

(1) that the drop of water is 0.05 gram in mass (m);

(2) that the impact pressure of the drop striking the cloth is exerted over an area (a) of 0.1 square centimeter in a direction perpendicular to the surface of the cloth;

(3) that the impact, or change in velocity (v), of the drop occurs in 0.001 second (t), which is approximately the time interval between the instant when the drop

first touches the fabric and the instant when the last part of the drop strikes the fabric if the velocity and mass are those mentioned; and

(4) that all the kinetic energy of the falling drop is used to produce a force manifested as a pressure on the striking area, instead of some being dissipated in spreading the drop or moving the fabric. Then the pressure exerted by the impact may be estimated by

$$P = \frac{mv}{ta} \qquad (3)$$

(This formula may be simply derived from the basic equations of moving bodies as outlined in any physics textbook.)

$$P = \frac{0.05 \times 340}{0.001 \times 0.1} = 170{,}000 \text{ dynes per square centimeter}$$

= approximately 170 centimeters of water pressure

By Eq. 2 this pressure would be great enough to drive the water through an opening approximately 0.001 cm. in diameter if the contact angle were 120 degrees.

In actual practice the pressure exerted by the falling drop upon the fabric may differ greatly from the value estimated above. Much of the kinetic energy of the drop probably is dissipated in spreading the drop when it strikes. The cloth, moreover, may be soft and elastic so that the time of impact is lengthened and some of the energy of the drop is absorbed in bending the fibers or moving the fabric instead of in forcing the water through the available capillaries. On the other hand, rain drops falling from considerable altitude undoubtedly have a greater velocity and a greater mass than those used in the calculation just made. It is not surprising, then, to observe small drops of water driven through tent or umbrella fabrics in a hard rainstorm.

Slowinske (11) and others (12) have shown that the backing applied to a fabric is an important factor in its efficiency as a water-repellent material. A soft cushion backing increases the ability of the material to withstand a hard rain because the energy of the falling drops is absorbed gradually, that is, the duration of impact (t in Eq. 3) is longer, and therefore the effective pressure is less. The effectiveness of a cushion depends further upon whether or not it is water-repellent, as illustrated by the following alternate suppositions:

1. If the cushion material is not water repellent it will absorb any drops driven through the outer fabric until the cushion becomes saturated. It will then pass the excessive water to the surroundings. In case the outer layer is not very water-repellent, some droplets may form on the under side, as illustrated in III and IV, Figure 3. If the cushion material touches these drops it will behave as a blotter and draw more and more water through the macrochannels of the outer fabric, thus hastening the complete wetting of the cushion layer.

2. If the cushion material is water-repellent any drops driven through the outer fabric will be trapped in the space between the cushion and the outer fabric, since by the time the water reaches this point it will have lost most of its kinetic energy of motion. The cushion itself is not absorbent so the drop will remain until it evaporates away. This explains the excellent rain protection afforded by a double fabric in which both layers are of water-repellent material.

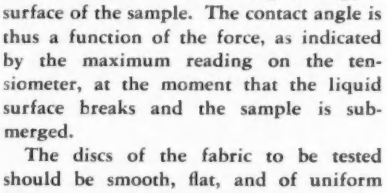
THE TENSIOMETRIC METHOD

The foregoing discussion has emphasized the importance of the contact angle as a factor in designing and testing a water-repellent fabric. The method of measuring the contact angle in most applications, however, requires the use of special optical equipment and is not conducive to rapid routine testing. A quick dynamic method of contact-angle evaluation for fabrics, in which a Cenco-Du Noüy interfacial tensiometer is used, has recently been described by two of us (13) and is briefly outlined below.

In this method the sample in the form of a circular disc one-half inch in diameter is adjusted to a position parallel to the surface of the water and is then pressed with gradually increasing force down into the water (see Figure 5). As the sample is pushed down, the angle formed by the edge of the water with the upper surface of the fabric gradually increases. The maximum angle attained is the contact angle. When the sample is pushed down further, the hydrostatic pressure of the water at the edge of the sample causes the water to move across the exposed upper surface of the sample. The contact angle is thus a function of the force, as indicated by the maximum reading on the tensiometer, at the moment that the liquid surface breaks and the sample is submerged.

The discs of the fabric to be tested should be smooth, flat, and of uniform diameter, and are best made by being stamped out with a one-half inch circular die on a hardwood block. They should never be touched by the hands but should be kept clean and free from surface contamination by being handled with a pair of clean forceps.

Figure 5. Diagram of cross section through disc being pressed into water surface.



The sample is held during the measurement by means of a slightly smaller metallic disc attached to the end of a rod, as shown in Figure 5. The underside of the metal disc is treated with a trace of adhesive (removed from the back of surgical tape after it is softened by warming) so that when the disc, properly centered and horizontal, is made to touch the flat circular sample uniformly, the latter adheres to the metallic disc and protrudes evenly from the circumference of the disc. The disc with the sample attached is then placed in the tensiometer so as to supplant the platinum ring normally used for surface tension measurements. The upper stage of the instrument is next lowered until the sample is just over the center of the water in a dish on the tensiometer platform. With the torsion wire and lever arm of the tensiometer unclamped, the water surface is now gradually raised and the sample carefully forced down by increasing downward tension until the water surface curls over the edge of the sample, while the pointer of the lever arm is kept in a balanced position up to the moment of break. The maximum tension observed before the sample breaks through the surface of the liquid is the value used in determining the contact angle.

The several readings made on each cloth are averaged, and a correction for the buoyant effect of the cloth is applied to the average value. For this correction the volume of the circular piece of cloth is calculated from its measured dimensions, and the weight of a corresponding volume of water (expressed as gravitational force in dynes) is subtracted from the measured force (in dynes). The correction may also be applied directly to the tensiometer reading. The following formulas, in which d is the diameter of the cloth sample and h is the gauge or thickness of the fabric (both in inches), may be used to make the calculations.

For the correction in dynes

$$C \text{ (dynes)} = 12{,}580\ d^2\ h$$

For the correction in tensiometer readings

$$C \text{ (t.r.)} = 1{,}049\ d^2\ h$$

The contact angle corresponding to the corrected tensiometer reading for fabric discs of one-half inch diameter can be read directly from the curve in Figure 6, which is obtained by plotting the data in Table I. The derivation of this relation between tensiometer reading and contact angle is shown in the original description of the tensiometric method (13). The tensiometer reading may be used directly without conversion into dynes if the tensiometer is calibrated according to the manufacturer's directions for rings of 6.00 cm. mean circumference.

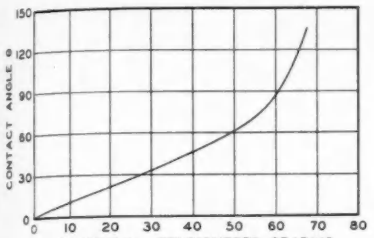


Figure 6. Tensiometer reading versus contact angle.

Table I. Tensiometer Readings and Corresponding Contact Angles
(For a sample with no buoyancy correction)

Tensiometer Readings: Scale Divisions	Dynes	Contact Angle Θ
20	240	21°
30	360	33
40	480	46
50	600	61
55	660	70
60	720	87
62	744	96
64	768	108
66	792	121
68	816	(142)*

* Extrapolated

Table II. Typical Data for the Evaluation of Contact Angles of Water-Repellent Fabrics by the Tensiometric Method

	Fabric A	Fabric B	Fabric C
Tensiometer Readings	54.5	68.2	66.4
	55.2	68.8	65.7
	52.8	69.2	66.0
	53.6	68.2	66.2
	55.5	69.4	65.4
	54.2	68.8	66.4
	57.2	69.4	66.2
	53.1	68.3	66.3
	56.0	68.5	66.7
	56.4	69.1	66.0
Mean	54.8	68.8	66.1
Average Deviation from Mean	1.4	0.4	0.3
Corresponding Contact Angle Deviation	1.5°	2.0°	1.5°
Corrected for Buoyancy	51.2	64.0	61.6
Contact Angle (Tensiometric)	63°	108°	94°

Typical results for three fabric samples are shown in Table II to illustrate the reproducibility of the tensiometer readings for the same sample.

Details concerning the precautions necessary to obtain accurate and reproducible results are also discussed in the original paper (13).

EXPERIMENTAL

Tests for water repellency were made on 26 experimentally and commercially prepared cotton fabrics described in Table III. Samples 1 to 8, inclusive, were treated in this laboratory with a commercial water repellent of the nondurable type. The method used was similar to common commercial practice but modified in such a way that different amounts of the finish, as indicated by the percentage figures in column 4 of Table III, were taken up by the cloth. The remaining samples were prepared by various manufacturers of commercial water-repellent fabrics using nondurable, semidurable and durable finishes.

TABLE III. SUMMARY OF TEST DATA ON FABRICS

Sample No.	Fabric	Finished-goods Specifications (See Note)	Finish	Spray-test Rating	Hydrostatic Pressure Reading (cm.)	Densometer Reading for Permeability to air (sec.) × (sec.)	Contact Angle (Degrees)
1	Print Cloth	88/ 76, 3.3, 1/1	A—¼%	0	0	5.0	56
2	Print Cloth	88/ 76, 3.3, 1/1	A—½%	50	4.0	5.4	94
3	Print Cloth	88/ 76, 3.3, 1/1	A—1%	70	12.0	5.3	99
4	Print Cloth	88/ 76, 3.3, 1/1	A—3%	90	18.0	5.2	121
5	Print Cloth	72/ 58, 2.6, 1/1	A—2%	90	10.0	3.1	114
6	Print Cloth	78/ 70, 3.0, 1/1	A—2%	100	14.0	4.4	114
7	Print Cloth	88/ 76, 3.3, 1/1	A—2%	80	18.0	7.4	117
8	Twill	104/ 60, 5.2, 1/1	A—2%	90	23.5	14.4	117
9	Poplin	110/ 54, 6.0, 2/1	B	50	10.0	64.6	90
10	Poplin	108/ 55, 6.3, 2/1	B	100	48.0	92.6	112
11	Poplin	112/ 52, 6.3, 1/1	B	100	48.0	88.2	112
12	Poplin	112/ 52, 6.3, 1/1	B	100	45.5	80.6	111
13	Poplin	108/ 52, 6.0, 2/1	C	100	28.5	42.7	112
14	Poplin	110/ 55, 6.0, 2/1	D	100	28.0	42.2	112
15	Poplin	108/ 52, 6.0, 2/1	E	100	30.5	27.5	110
16	Poplin	108/ 55, 6.0, 2/1	F	100	30.0	46.3	112
17	Poplin	106/ 57, 6.0, 2/1	G	100	32.0	59.2	113
18	Poplin	108/ 50, 6.0, 2/1	H	100	28.0	54.5	112
19	Poplin	108/ 52, 6.0, 2/1	I	100	36.0	61.6	114
20	Poplin	108/ 52, 6.0, 2/1	J	100	23.5	58.4	108
21	Poplin	108/ 51, 6.6, 1/1	K	90	33.0	55.1	112
22	Twill	144/ 98, 5.4, 2/2	E	100	51.0	68.0	111
23	Sheeting	64/ 53, 3.6, 1/1	K	80	11.0	4.6	112
24	Sheeting	64/ 53, 3.6, 1/1	C	80	12.0	4.1	109
25	H. B. Twill	60/ 46, 8.7, 1/1	K	90	26.5	23.6	110
26	Balloon Cloth (Substitute)	100/108, 3.0, 1/1	K	100	21.5	6.2	112

NOTE: First item, (e.g. 88/76), Finished warp and filling count.
Second item, (e.g. 3.3), Finished weight in ounces per sq. yd.
Third item, (e.g. 1/1), Warp and filling yarn ply.

The code letters in column 4 of Table III indicate which samples had the same type of finish.

Spray-test ratings, hydrostatic pressure measurements, Gurley Densometer air-permeability readings, and tensiometric contact angles were obtained for each of these fabrics. The results are shown in the last four columns of Table III and are charted in Figure 7 to show the correlation between the values for these four tests.

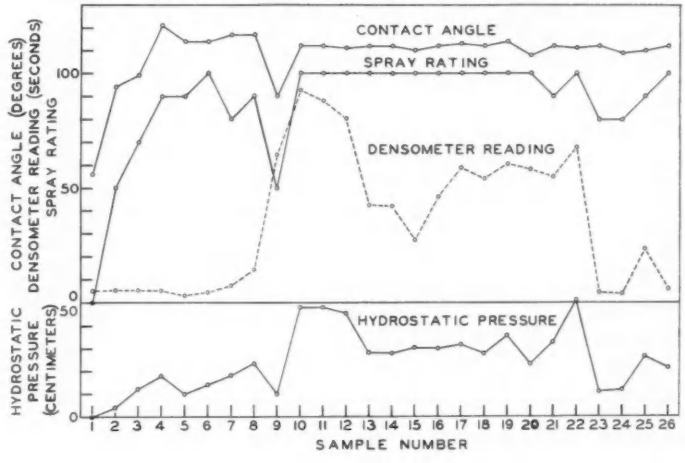
DISCUSSION

A study of the data in Table III and Figure 7 will bring out four interesting points, which warrant discussion:

1. Samples 1, 2, 3, 4, and 7 were prepared from the same original fabric, had the same construction, and gave approximately identical densometer readings; but the results for spray rating, hydrostatic pressure, and contact angle increased in a regular manner with the percent of water-repellent material applied to the cloth. This indicates that, other things being equal, the water repellency of the sample is, up to a certain point, a function of the concentration of finish on the fabric.

2. The hydrostatic pressure value of a fabric, in general, is directly related to the Densometer air-permeability value for a given surface finish. This is brought out by the data on samples 5 to 8, inclusive, and on samples 9 to 21, inclusive. The first group, for example, consisted of fabrics that were treated to have 2 percent of finish A, and thus to have approximately equal contact angles. An increase of hy-

Figure 7. Graphical representation of test data in Table III.



drostatic pressure required for penetration of these samples by water follows systematically the increase in Densometer values for permeability to air. This relationship is also more or less true of the poplin fabrics in the second group. Sample 9 is seemingly an exception to this generalization, for although it was treated with the same type of finish as samples 10, 11, and 12 its spray-test rating and hydrostatic pressure value were low in spite of its high Densometer reading. However, the low contact angle indicates that the finish may have been improperly applied; this would account for the poor water repellency of the fabric.

3. Samples 9 to 21, inclusive, were poplins of approximately the same construction and finished weight; yet their porosities to air as read by the Densometer varied over a wide range. It seems unlikely that this variation was due to the difference in the amounts of the finishing materials deposited on the fabrics. On examination of the two extremes, samples 10 and 15, it was found that sample 10 had an opaque, matted appearance, whereas sample 15 had numerous small openings clearly visible when the fabric was held up to the light.

It appeared that this difference might be explained by the tightness of the twist in the warp and filling yarns. Four samples, selected to represent the range of Densometer readings, were therefore subjected to twist analyses, results of which are shown in Table IV.

Table IV. Comparison of Yarn Twist With Densometer Readings on Fabrics

Sample No.	Warp Ply Twist	Warp Singles Twist*	Filling	Densometer Reading
	t.p.i.**	t.p.i.	t.p.i.	secs.
10	16.3	2.8	11.8	92.6
14	15.6	8.0	13.1	42.2
15	14.7	9.9	12.8	27.5
19	14.8	9.9	13.4	61.6

* This figure is the twist in the singles yarn as it rests in the ply.
** Turns per inch.

The results for samples 10, 14, and 15 seemed to indicate that the difference in Densometer readings might be a function of the twist. Sample 15, which gave the very low Densometer reading of 27.5 seconds, had the tightest twist while sample 10, with the very high reading of 92.6 seconds, had a very loose twist. Sample 19, however, was inconsistent in this respect, and gave a fairly high Densometer reading in spite of a high twist. This shows that other factors are involved, probably factors in the manufacture and finishing which tend to close up the large macrochannels.

It was pointed out in connection with Equation 2 that the hydrostatic pressure necessary to force water through the capillary is inversely proportional to its diameter. It follows that the hydrostatic pressure test value is a function of the diameter of the macrochannels through the fabric. For a material of given weight a lower twist multiple will result in a slight increase in the diameter of the microchannels with a concomitant decrease in diameter of the macrochannels. This probably explains the high hydrostatic pressure value of Samples 10, 11, and 12. Thus a simple change in the construction of a fabric appreciably improves its efficiency as a water-repellent material.

4. Some finished fabrics with high contact angles had spray-test ratings of less than 100 (Samples 4, 5, 7, 8, 23, and 24). These cloths in general had low Densometer readings, showing that the openings are relatively large and indicating that, contrary to generally accepted belief, the spray-test rating may depend somewhat upon the construction and weight of the fabric. The finishes on these fabrics, however, were all of the semidurable or nondurable type, which may be responsible for a lower spray rating if some of the finish is washed off during the first part of the spraying.[1] This fact might explain the apparent discrepancy between the contact angle and spray rating results observed for the above mentioned samples. The contact angle measurement is made at the initial contact between the fabric and water, whereas the spray-test rating is taken on the sample after it has been subjected to considerable spraying.

It was observed in this connection that after spray-test ratings were determined on an open fabric, such as sample 23, water adhered to the back of the sample at the points where water appeared to wet the sample on the front side. This suggests the possibility of a "mechanical adhesion," which holds the water on the surfaces of the fabric by means of the water filling the larger openings. The cohesion between the water in these macrochannels and the water on the surface might be sufficiently great to hold the water on the surface in spite of tapping, to give the fabric a wet appearance and, consequently, a low spray-test rating even though the contact angle is high.

The evidence presented in this discussion of water repellency leads to the conclusion that no single laboratory test is sufficient to characterize or evaluate the efficiency of a water-repellent fabric. Each test measures some property or combination of properties different from those measured in another test. The contact angle seems to be the most specific test in that it evaluates primarily the waterproofing finish on the fibers and yarns.

The more efficient water-repellent, single-layer fabrics by laboratory criteria would be those that rated high in all four tests described above. Samples 10, 11, 12, and 22 fall in this classification. These fabrics have the essential characteristics—close weaves and good finishing treatments.

Recent practice has demonstrated the usefulness of physico-chemical principles in the development of improved water-repellent fabrics. The idea of decreasing the size of the macrochannels in fabrics by using lower twist multiples in the yarns has already found practical application in the trade. The use of a soft, water-repellent backing behind the outside fabric which comes in contact with water has also been shown to be basically sound. These improvements indicate that further progress may be made by those giving close consideration to the fundamental principles involved in wetting action.

SUMMARY

1. Some theoretical aspects of water repellency in treated fabrics have been reviewed. The significance of contact angle has been pointed out, and the importance of the size of the openings in such fabrics has been demonstrated.

2. A tensiometric method of evaluating the contact angle of water with fabric surface has been described.

3. The constructions, spray-test ratings, hydrostatic pressures, Gurley Densometer air-permeability values, and tensiometric contact angles for 26 experimental and commercial fabrics have been compared. From these data a number of interesting facts have been learned concerning constructions and treatments that contribute toward efficient water-repellent fabrics.

4. It is concluded that adequate evaluation of water-repellent fabrics requires testing by each of the four methods described.

ACKNOWLEDGMENT

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[1] G. A. Slowinske, who kindly reviewed this manuscript for the authors, has pointed out in a private communication that in the spray rating test "some fabrics or finishes will resist wetting during the first 5-10 seconds of the spraying, but will become wetted towards the end of the spraying. This has suggested that the water resistance of a fabric, or its contact angle, may be influenced by the time of contact between fiber and water." The authors have observed this effect for fabrics with nondurable finishes.